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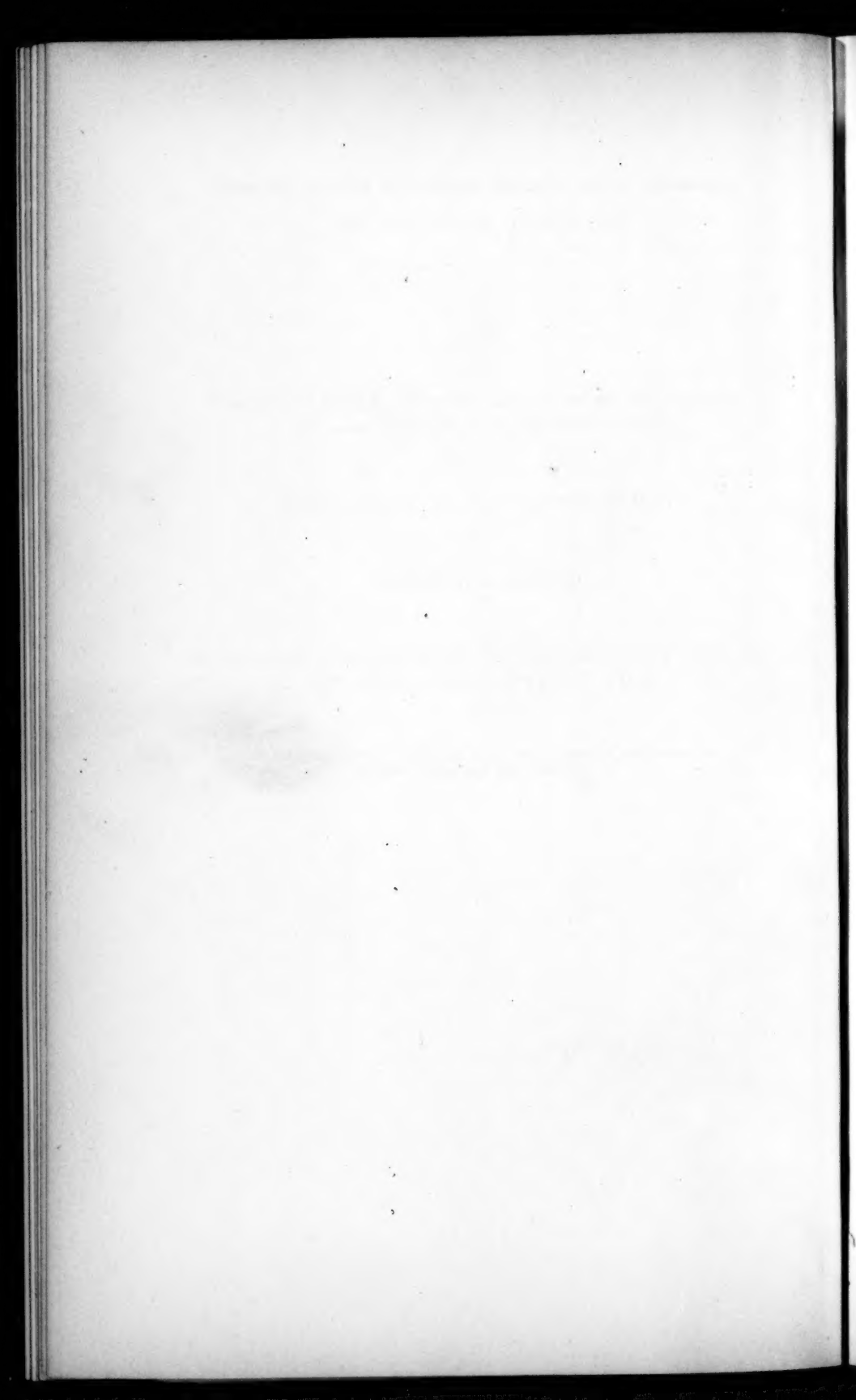
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
CASE SCHOOL OF APPLIED SCIENCE. — XII.

THE COMPOSITION OF PETROLEUM.

BY CHARLES F. MABERY.

*ON THE HYDROCARBONS IN PENNSYLVANIA PETROLEUM
WITH BOILING POINTS ABOVE 216°.*

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In a former paper* the principal hydrocarbons in Pennsylvania, Ohio, and Canadian petroleum below 216°, were shown to have the composition represented by the general formula C_nH_{2n+2} . Concerning the constituents with higher boiling points very little is known. Pelouze and Cahours† collected distillates to which they gave the following formulas:—

216°–218°	236°–240°	255°–260°	280°
$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$

From paraffine the following hydrocarbons have been separated (Beilstein's Handbook):—

212°–215°	230°–235°	252°–255°	273°–275°
$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$

So far as I am aware, these are the only allusions to the composition of Pennsylvania petroleum in these portions. It appears that the distillations were made under ordinary atmospheric pressure in presence of air with no attempts to avoid decomposition under these conditions.

Then, furthermore, as I have suggested in a former paper, the high specific gravity of the distillates separated by Pelouze and Cahours indicate that their distillates were obtained from Canadian petroleum. It does not appear that any attempts have been made to ascertain the molecular weights of the individual hydrocarbons. Indeed this has been

* These Proceedings, XXXII. 121.

† Ann. Chim. Phys. (4), 1, 5 (1864).

possible only within recent years since the freezing and boiling point methods for the determination of molecular weights have been known. Then it is not possible to determine the vapor densities of these hydrocarbons, because, as I have recently ascertained, even in vacuo small quantities of the hydrocarbons such as are used in vapor density determinations, undergo serious decomposition; and this occurs even in oils that have been distilled many times over in bulk in vacuo. In the earlier work, it was evidently assumed that a few distillations under atmospheric pressure were sufficient to collect the individual hydrocarbons within the limits of their boiling points, sufficient at least to afford reliable data as to their composition. A glance at the small differences in percentage composition is sufficient to show that it is not possible by analysis alone of products even well purified to distinguish between homologous members of a series, although such analysis may define the series.

But the chief difficulty is to obtain each hydrocarbon uncontaminated by any admixture of its homologues or by products of decomposition. This is well illustrated by the experience of Markownikoff in separating the hydrocarbons in the Russian oil, who found it impossible to collect distillates closer than limits of five degrees on account of decomposition. That the same is true perhaps in a less degree in distillates from Pennsylvania oil is evident whenever distillation is made of the higher portions under atmospheric pressure. The rank odor is evidence of cracking. Yet the constituents with higher boiling points are under the influence of vapor tension as much as the constituents with lower boiling points, and consequently require as prolonged distillation for complete or approximately complete separation. In my experience it is only possible to obtain even an approximate separation by exclusion of air and depression of boiling points.

In this manner the higher hydrocarbons may be distilled any number of times with no appreciable decomposition. The only limit is the patience of the operator. But the stability of these hydrocarbons is evidently dependent on the influence of mass. Since as mentioned above, while distillation of any considerable quantity of the oil may be carried on indefinitely, a limited quantity cannot be volatilized even in vacuo without decomposition. Many attempts to determine the vapor density of the hydrocarbons in Pennsylvania and California petroleum by volatilization in vacuo according to the method of Lunge and Neuberg have failed on account of cracking, even so far as the separation of sooty carbon from the members with high boiling points.

In September, 1896, I set out to ascertain the composition of the principal hydrocarbons in Pennsylvania petroleum above 216° so far as they can be separated by distillation on a laboratory scale. Through the courtesy of the Standard Oil Company, I procured a barrel of crude oil from Oil City and this material has been used to separate the hydrocarbons that will be described in this paper. That this oil was an approximately average specimen of Pennsylvania petroleum, appears from its properties. A determination of the specific gravity of the crude oil at 20° gave 0.8095. A combustion of the oil dried over sodium gave the following percentages of carbon and hydrogen: Carbon, 85.80; Hydrogen, 14.04. Eight hundred grams distilled in the ordinary way in the following proportions: —

50° – 150°	150° – 200°	200° – 250°	250° – 300°	$+300^{\circ}$
166	88	83	100	337

Fifty-six kilos of the crude oil was distilled in quantities of 10 litres each in a porcelain still, collecting under atmospheric pressure to 200° , and within limits of 10° under a vacuum of 50 mm. to 300° , then within limits of 5° , and finally within limits of 2° . After eight distillations the following proportions collected: —

124° – 126°	136° – 138°	156° – 158°	174° – 176°	188° – 199°
Grams, 125	145	240	205	240
199° – 201°	210° – 212°	226° – 228°	242° – 244°	
225	335	150	130	

Since the weights of these fractions represent all that came from the original crude oil, it is possible to gain a very general idea of the proportion of the hydrocarbons which are contained in the crude oil. But such estimation must be only approximate from the fact that any distillation however thorough gives only an approximate separation, and a considerable portion of any hydrocarbon must be contained in the intermediate distillates.

The percentages of the weights are as follows: —

$C_{13}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{34}$	$C_{17}H_{36}$
124° – 126°	136° – 138°	156° – 158°	174° – 176°	188° – 199°
0.22	0.26	0.43	0.37	0.43 per. cent.
$C_{18}H_{38}$	$C_{19}H_{40}$	$C_{20}H_{42}$	$C_{21}H_{44}$	
199° – 201°	210° – 212°	230° – 232°	242° – 244°	
0.40	0.60	0.27	0.23 per. cent.	

In the intervals between these fractions the weights were much smaller.

After the eighth distillation each fraction was agitated at first with common concentrated sulphuric acid until the acid was not much colored and then several times with fuming sulphuric acid. That the distillates consist almost entirely of the principal hydrocarbon is shown by the slight change in specific gravity by the acid treatment:—

156°–158°	174°–176°	182°–184°	
0.805	0.8064	0.8100	Original distillate.
0.7992	0.8031	0.8093	After treatment with acid.

There was some loss in weight of the fraction by the acid treatment, but it was doubtless due for the most part to solution of the principal hydrocarbons in the acid. The weights of the fractions before and after treatment were as follows:—

156°–158°	174°–176°	182°–186°
240	215	205
195	190	155

This solvent action has been observed in other oils with high boiling points in continuous treatment with fuming sulphuric acid, which caused a gradual loss without changing materially the specific gravity. After the purification with the acid, distillation was continued through a Hempel column filled with glass beads or broken glass, under 50 mm. within limits of one degree, until the hydrocarbons collected in considerable quantities. After the thirtieth distillation, the hydrocarbons came together within the following limits:—

124°–126°, 142°–143°, 158°–159°, 173°–174°, 189°–190°, 198°–199°.

Even after nearly continuous distillation of sixteen months, these products showed very little indication of decomposition. Leaks in the apparatus immediately cause decomposition, as shown by a disagreeable odor, and the appearance of the distillates. So long as air is excluded from the hot vapors there is no danger of decomposition. But as we found in attempting to ascertain the boiling points under atmospheric pressure, a single distillation in air causes a very rank odor of decomposition.*

* The difference in stability of the constituents of different petroleum is shown by their behavior when air comes in contact with the hot vapors. In accidents that have occurred during distillation, letting in air on the hot vapors, in the case of Pennsylvania petroleum the still becomes filled with dark vapors, but in a

In determining the boiling points of these hydrocarbons under atmospheric pressure, 70 grams of the fraction 124°–126° distilled as follows, under 760 mm. and with the mercury column all within the vapor: —

	224°–225°	225°–226°	226°–227°	227°–228°	228°–229°
Grams,	4	28	26	3	3
	Colored residue, 6				

The portions between 225° and 227° collected almost entirely between 225°.5 and 226°.5.

The fraction 142°–143° nearly all distilled at 237°–238° atmospheric pressure, the fraction 158°–159° at 256°–257°, the fraction 173°–174° at 274°–275°, the fraction 188°–189° at 288°–289°, and the fraction 198°–199° at 300°–301°. The hydrocarbon dodecane $C_{12}H_{26}$ was identified in the fraction 214°–216°.*

TRIDECANE, $C_{13}H_{28}$.

The next homologue, tridecane, was sought for in the series of distillates that collected between 215° and 235°. After carrying these fractions eight times through a Hempel bead column a larger portion, 200 grams, collected at 221°–222°. This portion was distilled twenty-four times, when 70 grams collected, as shown above. The specific gravity of the distillate before further treatment was 0.7866, and after thorough agitation with fuming sulphuric acid, 0.7834. A combustion gave the following values for carbon and hydrogen: —

0.1506 grm. of the oil gave 0.4690 grm. CO_2 and 0.2028 grm. H_2O .

	Calculated for $C_{13}H_{28}$.	Found.
C	84.78	84.94
H	15.22	14.96

The molecular weight of this oil as determined by the Beckman method at the freezing point of benzol, in the hands of different workers, corresponded to that of $C_{13}H_{28}$.

distillation of Russian petroleum, air accidentally admitted caused such a violent explosion that the thermometer was sent violently across the room and broken against the wall.

* These Proceedings, XXXII. 138.

- I. 1.1209 grm. of the oil and 36.3043 grms. benzol gave a depression of $0^{\circ}.82$.
- II. 1.2502 grm. of the oil and 33.3631 grms. benzol gave a depression of $1^{\circ}.015$.
- III. 1.496 grm. of the oil and 32.9131 grms. benzol gave a depression of $1^{\circ}.205$.

Calculated for $C_{18}H_{38}$	I.	Found. II.	III.
184	184.5	181	184.9

In still further confirmation of the formula of tridecane, the index of refraction was determined, and its molecular refraction calculated. The index was found to be 1.4354 at 20° , and the molecular refraction as follows:—

Calculated for $C_{18}H_{38}$	Found.
61.94	61.44

Monochlorotridecane, $C_{18}H_{37}Cl$. — In the preparation of the chlorine derivative of tridecane, chlorine was allowed to act on the hydrocarbon in screened sunlight, over water. With care to avoid an excess of chlorine, the product consisted for the most part of the monochloride. It was fractioned in vacuo under 12 mm. several times until considerable of the oil collected at 135° – 140° . This fraction gave as its specific gravity at 20° , 0.8973. A determination of chlorine gave a percentage required for the monochloride:—

0.1920 grm. of the oil gave 0.1273 grm. AgCl.

	Required for $C_{18}H_{37}Cl$.	Found.
Cl	16.23	16.39

The molecular weight as determined at the freezing point of benzol corresponded to the same formula:—

0.4585 grm. of the oil and 18.35 grms. benzol gave a depression of $0^{\circ}.568$.

Calculated for $C_{18}H_{37}Cl$.	Found.
218.5	216

A determination of the index of refraction confirmed the same formula; the index as determined was 1.451, corresponding to the molecular refraction:—

Calculated.	Found.
65.71	66.67

TETRADECANE, $C_{14}H_{30}$.

The fraction 142° – 143° , collected after the twenty-fourth distillation, gave as its specific gravity, after drying over sodium, 0.7848. After agitating with concentrated sulphuric acid, washing, and drying over sodium, it gave 0.7847. After treatment with fuming sulphuric acid it gave 0.7814; this determination, like the others, was made at 20° .

A determination of the molecular weight of this fraction purified with fuming sulphuric acid gave the following result:—

- I. 1.1049 grm. of the oil and 36.8505 grms. benzol gave a depression of $0^{\circ}.735$.
- II. 1.052 grm. of the oil and 35.970 grms. benzol gave a depression of $0^{\circ}.718$.

Calculated for $C_{14}H_{30}$.	Found.	
	I.	II.
198	199.9	199.5

A combustion gave the following percentages of carbon and hydrogen:

0.1502 grm. of the oil gave 0.4698 grm. CO_2 and 0.2024 grm. H_2O .

	Calculated for $C_{14}H_{30}$.	Found.
C	84.84	85.02
H	15.16	14.96

This specimen was purified with common concentrated acid; another portion purified with fuming sulphuric acid gave slightly different proportions:—

0.1458 grm. of the oil gave 0.4532 grm. CO_2 and 0.1970 grm. H_2O .

	Calculated for $C_{14}H_{30}$.	Found.
C	84.84	84.76
H	15.16	15.02

The boiling point of this fraction under 760 mm. was 236° – 238° . On account of decomposition when the oil is distilled in air, it is difficult to determine the boiling point with great precision.

A determination of the index of refraction of this hydrocarbon gave 1.4360, which corresponds to the following molecular refraction:—

Calculated or $C_{14}H_{30}$.	Found.
66.54	66.36

Monochlortetradecane, $C_{14}H_{29}Cl$. — Since only small quantities of the purified hydrocarbons were available for the study of the chlorides, great care was necessary to avoid too high chlorination. Most of the hydrocarbons gave only sufficient of the chlorine derivative to verify its formula by the percentage of chlorine. The chlorine product obtained from tetradecane was fractioned in vacuo until it collected in larger quantities at 150° – 153° under 20 mm. A determination of chlorine gave the following result:—

0.1966 grm. of the oil gave 0.1245 grm. AgCl.

	Calculated for $C_{14}H_{29}Cl$.	Found.
Cl	15.25	15.65

Its specific gravity at 20° was found to be 0.9185. The quantity of product was not enough for other determinations. Another portion of the chlorine product collected at 175° – 180° , 17 mm., which gave as its specific gravity at 20° , 1.032. A determination of chlorine gave the value required for the dichloride:—

0.1937 grm. of the oil gave 0.2125 grm. AgCl.

	Calculated for $C_{14}H_{29}Cl_2$.	Found.
Cl	26.55	27.12

A determination of molecular weight at the freezing point of benzol confirmed the dichloride:—

1.3407 grm. of the oil and 19.81 grms. benzol gave a depression of $1^{\circ}.255$.

	Calculated for $C_{14}H_{29}Cl_2$.	Found.
	267	264.3

PENTADECANE, $C_{15}H_{32}$.

The specific gravity of the fraction 158° – 159° (50 mm.) dried over sodium was found to be 0.8054 at 20° . After treatment with concentrated sulphuric acid it gave 0.7939, and after thorough treatment with fuming sulphuric acid it gave 0.7896.

The molecular weight was determined by the Beckman method:—

- I. 1.050 grm. of the oil and 35.9775 grms. benzol gave a depression of $0^{\circ}.675$.
- II. 1.3946 grm. of the oil and 23.2679 grms. benzol gave a depression of $1^{\circ}.37$.

	Calculated for $C_{15}H_{32}$.	I.	Found.	II.
	212	211		212

Combustion I. was made of the unpurified distillate dried over sodium; and combustion II., of the oil after treatment with fuming sulphuric acid:—

- I. 0.1440 grm. of the oil gave 0.4500 grm. CO_2 and 0.1919 grm. H_2O .
 II. 0.1608 grm. of the purified oil gave 0.5002 grm. CO_2 and 0.2198 grm. H_2O .

	Calculated for $\text{C}_{15}\text{H}_{32}$.	Found.	
		I.	II.
C	84.92	85.21	84.87
H	15.08	14.80	15.20

In determining the boiling point of pentadecane under atmospheric pressure, it distilled almost completely at 256° – 257° .

A determination of the index of refraction gave 1.4413, from which the molecular refraction was calculated:—

Calculated for $\text{C}_{15}\text{H}_{32}$.	Found.
71.15	70.49

Dichloropentadecane, $\text{C}_{15}\text{H}_{30}\text{Cl}_2$.—With the small quantity of the hydrocarbon at hand, we did not succeed in limiting the action of chlorine to the formation of the monochloride. Fractioned in vacuo under 13 mm. the chlorinated product collected for the most part at 175° – 180° . This product gave as its specific gravity at 20° , 1.0045. A Carius determination for chlorine gave the following percentage:—

0.1411 grm. of the oil gave 0.1462 grm. AgCl .

	Calculated for $\text{C}_{15}\text{H}_{30}\text{Cl}_2$.	Found.
Cl	25.28	25.63

The molecular formula was established by a determination of its molecular weight:—

1.4308 grm. of the oil and 18.53 grms. benzol gave a depression of 1.336.

Calculated for $\text{C}_{15}\text{H}_{30}\text{Cl}_2$.	Found.
281	283.2

HEXADECANE, $\text{C}_{16}\text{H}_{34}$.

The heap that collected at 174° – 175° , 50 mm., after the thirtieth distillation gave as its specific gravity at 20° , 0.8000. After treatment with concentrated sulphuric acid it gave 0.7964, and after treatment with fuming sulphuric acid, 0.7911. It distilled almost completely at 275° –

276° under 760 mm., barometric pressure. In determining the molecular weight of this fraction at the freezing point of benzol, it gave the formula $C_{16}H_{34}$:—

- I. 1.1507 grm. of the oil and 35.27 grms. benzol gave a depression of 0°71.
 II. 1.1833 grm. of the oil and 35.63 grms. benzol gave a depression of 0.715.

Calculated for $C_{16}H_{34}$.	Found.	
	I.	II.
226	225.2	227.6

Determinations of carbon and hydrogen were made in the unpurified distillate (I.), in a portion purified with concentrated sulphuric acid (II.), and in a third portion purified with fuming sulphuric acid (III.), with the following results:—

- I. 0.1477 grm. of the oil gave 0.4600 grm. CO_2 and 0.1973 grm. H_2O .
 II. 0.1454 grm. of the oil gave 0.4522 grm. CO_2 and 0.1986 grm. H_2O .
 III. 0.1454 grm. of the oil gave 0.4516 grm. CO_2 and 0.1971 grm. H_2O .

	Calculated for $C_{16}H_{34}$.	Found.		
		I.	II.	III.
C	84.96	84.94	84.80	84.60
H	15.04	14.84	15.18	15.06

The index of this hydrocarbon was found to be 1.4413, from which the molecular refraction was calculated:—

Calculated for $C_{16}H_{34}$.	Found.
75.750	75.555

Dichlorhexadecane, $C_{16}H_{33}Cl_2$.—The chlorine product obtained from hexadecane collected for the larger part at 205°–210°, under 16 mm. Its specific gravity was 1.0314 at 20°. A determination of chlorine gave a value required for the dichloride:—

0.1477 grm. of the oil gave 0.1525 grm. $AgCl$.

	Calculated for $C_{16}H_{33}Cl_2$.	Found.
Cl	24.61	24.44

This formula was also confirmed by its molecular weight:—

0.5019 grm. of the oil and 18.21 grms. benzol gave a depression of 0°.457.

Calculated for $C_{16}H_{33}Cl_2$.	Found.
295	295

A portion of the original distillate 174° – 175° was cooled to -10° , which caused the separation of a crystalline mass. It was filtered cold, but the solid remaining formed but a small part of the original oil.

The specific gravity of the filtered oil 0.8005, was slightly higher than the unfiltered distillate. The quantity of the solid was not sufficient for analysis or further examination. No further examination was made of the filtered oil, for it was evident that the small amount of solid hydrocarbon could not change the composition, nor other constants, especially since, as shown above, the original distillate has the composition of the series C_nH_{2n+2} .

HEPTADECANE, $C_{17}H_{36}$.

The fraction which collected at 188° – 190° after the 42d distillation gave as its specific gravity at 20° after drying over sodium, 0.8017. After agitation with sulphuric acid it gave 0.8019, and after purification with fuming sulphuric acid, 0.8000. Under 760 mm. pressure this oil distilled almost entirely at 288° – 289° , with very little residue above 289° . The small residue was badly colored from decomposition. Evidently it would not be possible to distill this oil continuously under atmospheric pressure in presence of air without serious decomposition.

The formula of this distillate was established by two determinations of its molecular weight and by analysis.

- I. 1.4294 grm. of the oil and 25.7086 grms. benzol gave a depression of $1^{\circ}.17$.
- II. 1.4382 grm. of the oil and 25.6785 grms. benzol gave a depression of $1^{\circ}.18$.

Calculated for $C_{17}H_{36}$.	Found.	
	I.	II.
240	241.2	240.9

Analysis I. was made of the unpurified oil dried over sodium, and Analysis II. after purification with fuming sulphuric acid.

- I. 0.1534 grm. of the oil gave 0.4778 grm. CO_2 and 0.2044 grm. H_2O .
- II. 0.1491 grm. of the oil gave 0.4641 grm. CO_2 and 0.2014 grm. H_2O .

	Calculated for $C_{17}H_{36}$.	Found.	
		I.	II.
C	84.96	84.94	84.87
H	15.04	14.80	15.01

Monochlorheptadecane, $C_{17}H_{35}Cl$.—The chlorine product from heptadecane collected in considerable quantity at 175° – 177° , 15 mm. Its specific gravity at 20° was found to be 0.8962. The percentage of chlorine corresponded to the monochloride:—

0.1510 grm. of the oil gave 0.0807 grm. $AgCl$.

	Calculated for $C_{17}H_{35}Cl$.	Found.
Cl	12.92	13.21

On cooling a portion of the distillate 188° – 189° to -10° , it formed a pasty mass from which a small amount of a crystalline solid was obtained by filtration. The solid after crystallization from ether and alcohol melted at approximately 10° . The amount of solid was not sufficient for purification or examination. The filtered oil gave as its specific gravity at 20° , 0.8035, slightly higher than the distillate before filtration. Since the original distillate showed the composition of the series, C_nH_{2n+2} , it did not seem worth while to make any further examination of the filtered oil.

OCTODECANE, $C_{18}H_{38}$.

After the twenty-sixth distillation larger quantities of distillates collected between 198° and 204° , mostly at 199° – 200° (50 mm). The distillate 199° – 200° distilled for the most part, although with considerable colored residue and bad odor, at 300° – 301° , under 760 mm. After drying over sodium its specific gravity was 0.8054, after agitation with sulphuric acid, 0.8035, and after purification with fuming sulphuric acid, 0.8017, at 20° .

Its molecular weight was ascertained by the Beckman method at the freezing point.

- I. 0.9963 grm. of the oil and 36.4129 grms. benzol gave a depression of $0^{\circ}.53$.
- II. 0.9926 grm. of the oil and 23.2544 grms. benzol gave a depression of $0^{\circ}.84$.

Calculated for $C_{18}H_{38}$.	Found.	
	I.	II.
254	252.7	254.2

Combustion I. was made of the unpurified distillate dried over sodium; combustion II., of the oil after purification with concentrated sul-

phuric acid; and combustion III., after treatment with fuming sulphuric acid.

- I. 0.1423 grm. of the oil gave 0.4435 grm. CO_2 and 0.1915 grm. H_2O .
 II. 0.1513 grm. of the oil gave 0.4702 grm. CO_2 and 0.2054 grm. H_2O .
 III. 0.1524 grm. of the oil gave 0.4727 grm. CO_2 and 0.2064 grm. H_2O .

	Calculated for $\text{C}_{18}\text{H}_{38}$.	I.	Found. II.	III.
C	85.06	85.02	84.76	84.59
H	14.94	14.96	15.09	15.05

It is evident from the slight change in specific gravity after purification, and the percentages of carbon and hydrogen, that the original distillate consisted to a large extent of octadecane.

Monochlorooctadecane, $\text{C}_{18}\text{H}_{37}\text{Cl}$. — The product obtained by the action of chlorine on octadecane, collected in greater part at 185° – 190° , under 15 mm., and this fraction gave as its specific gravity at 20° , 0.9041. The percentage of chlorine corresponded to the monochloride:—

0.1482 grm. of the oil gave 0.0782 grm. AgCl .

	Calculated for $\text{C}_{18}\text{H}_{37}\text{Cl}$.	Found.
Cl	12.35	13.05

The results given above were obtained with the hydrocarbon that was liquid at ordinary temperatures. When it was found that crystals separated from this distillate at 3° , and that it became pasty at 0° , it was cooled to -10° , when it became so thick it filtered only slowly. The solid after filtering was melted and again cooled and filtered, after which it was perfectly white. It was then crystallized from ether and alcohol, after which it melted at 20° . It was estimated that twenty per cent of the original oil separated as the solid hydrocarbon on cooling. It was difficult to separate the solid completely on account of the great solvent action of the oil.

The filtered and pressed solid melted at 20° , and after crystallization from ether and alcohol and from gasoline, the melting point could not be raised. Krafft* gave 28° as the melting point of octadecane, which he obtained from stearic acid; but his octadecane boiled at $214^\circ.5$ under 50 mm. pressure. The specific gravity of the solid hydrocarbon was

* Ber. deutsch. chem. Gesellsch., XV. 1703 (1882).

0.7830 at 30° and 0.7816 at 40° . Krafft gave 0.7768 as the specific gravity of $C_{18}H_{38}$ at 28° . A determination of the molecular weight of the purified hydrocarbon confirmed its formula:—

1.1003 grm. of the oil and 19.65 grms. benzol gave a depression of 0.941.

Calculated for $C_{18}H_{38}Cl$.	Found.
288.5	291.5

This molecular weight, showing that the hydrocarbon boiling at 300° is octodecane, does not agree with Krafft's conclusion as to the formula of the hydrocarbon obtained from stearic acid. In heating stearic acid with hydriodic acid Krafft assumed that all the oxygen is removed, leaving intact the carbon of the carboxyl, with the formation of octodecane. But when this work was done the only means of verifying the formula was by analysis, which was sufficient to determine the series, but not the individual members of the series. While the results of Krafft's combustions gave almost exact values for the formula $C_{18}H_{38}$, the size of the molecule could not be determined. Krafft looked upon the hydrocarbon boiling at 303° as having the formula $C_{17}H_{36}$.

The specific gravity of the oil after cooling and filtration was somewhat higher than before, 0.8110 at 20° , and higher than the specific gravity of the filtered solid octodecane, 0.7830. The molecular weight of the filtered oil was the same as before filtration.

0.9904 grm. of the substance and 16.10 grms. benzol gave a depression of $1^{\circ}.184$.

Calculated for $C_{18}H_{38}$.	Found.
254	254.6

A combustion of the liquid hydrocarbon showed some change in the proportions of carbon and hydrogen:—

0.1483 grm. of the substance gave 0.4636 grm. CO_2 and 0.1954 grm. H_2O .

	Calculated for		Found.
	$C_{18}H_{36}$.	$C_{18}H_{38}$.	
C	85.70	85.06	85.25
H	14.30	14.94	14.64

While there is a narrow difference in calculated percentages between the two formulae, the percentages found, together with the higher specific gravity, indicate that the filtered oil was a mixture of the two series C_nH_n and H_nC_{n+2} .

A determination of the index of refraction, which was found to be 1.4435, and the molecular refraction, correspond more nearly to the formula $C_{18}H_{38}$:—

Calculated for		Found.
$C_{18}H_{38}$	$C_{18}H_{38}$	
82.90	84.96	82.60

A combustion of the solid hydrocarbon gave proportions required for the series C_nH_{2n+2} :—

0.1564 grm. of the substance gave 0.4883 grm. CO_2 and 0.2083 grm. H_2O .

	Calculated for $C_{18}H_{38}$	Found.
C	85.06	85.15
H	14.94	14.80

The position in the series was shown by its molecular weight:—

- I. 1.9475 grm. of the solid and 25.21 grms. benzol gave a rise of $0^{\circ}.7734$.
 II. 1.9475 grm. of the solid and 25.28 grms. benzol gave a rise of $0^{\circ}.7830$.

Calculated for $C_{18}H_{38}$	Found.	
	I.	II.
254	256	253.2

The formula of octadecane was further confirmed by its index of refraction. The index was found to be, at 20° , 1.440, which corresponds to the molecular refraction:—

Calculated for $C_{18}H_{38}$	Found.
84.96	84.53

NONODECANE, $C_{19}H_{40}$.

In the eighth distillation under 50 mm., 335 grams collected at 210° – 212° with much smaller weights on either side. After continuing the distillation twenty-seven times, a portion of the fraction 210° – 212° was purified with fuming sulphuric acid; before this treatment the oil gave as its specific gravity at 20° , 0.8274, and afterward, 0.8122. In determining its molecular weight by the freezing point method the following values were obtained:—

- I. 1.1039 grm. of the oil and 39.7462 grms. benzol gave a depression of $0^{\circ}.575$.
 II. 1.1418 grm. of the oil and 36.2175 grms. benzol gave a depression of $0^{\circ}.505$.

Calculated for $C_{10}H_{40}$	Found.	
	I.	II.
268	269.5	268

Determinations of carbon and hydrogen gave values for the series C_nH_{2n+2} :—

- I. 0.1530 grm. of the oil gave 0.4771 grm. CO_2 and 0.1994 grm. H_2O .
 II. 0.1591 grm. of the oil gave 0.4976 grm. CO_2 and 0.2132 grm. H_2O .

	Calculated for		Found.	
	$C_{10}H_{38}$	$C_{10}H_{40}$	I.	II.
C	85.70	85.08	85.04	85.29
H	14.30	14.92	14.48	14.89

Analysis I. was made of the oil before purification, and Analysis II. afterward.

A determination of the index of refraction gave 1.4522, which corresponds to the following molecular refraction:—

Calculated for $C_{10}H_{40}$	Found.
89.55	88.68

The results on the composition of the distillate 210° – 212° were obtained on the purified distillate without cooling to separate the solid hydrocarbon. On cooling a portion of this distillate to -10° , filtering cold and pressing the solid, 5 grams of the solid hydrocarbon, and 30 grams of the liquid hydrocarbon were obtained; the solid hydrocarbon, therefore, formed a small part of the original distillate. The specific gravity of the filtered oil was 0.8208 at 20° . The specific gravity of the distillate before cooling as shown above was 0.8122 at 20° .

After crystallization from ether and alcohol, the specific gravity of the solid hydrocarbon was 0.7725, 30° , and 0.7781 at 30° .

A determination of its molecular weight gave a value required for the hydrocarbon $C_{10}H_{40}$.

1.4011 grm. of the solid and 26.66 grms. benzol gave a rise of $0^{\circ}.496$.

Calculated for $C_{10}H_{40}$	Found.
268	271.6

The melting point of the solid was found to be 33° – 34° corresponding to the melting point, 32° , that Krafft found for the solid hydrocarbon distilling at, $226^{\circ}.5$, 50 mm.

A combustion of the oil filtered from the solid hydrocarbon gave percentages of carbon and hydrogen required for $C_{16}H_{38}$.

0.1495 grm. of the oil gave 0.4715 grm. CO_2 and 0.1928 grm. H_2O .

Calculated for $C_{16}H_{38}$.	Found.
85.70	86.00
14.30	14.33

A determination of the molecular weight confirmed the formula:—

2.5445 grms. of the oil and 24.63 grms. benzol gave a rise of $0^{\circ}.994$.

Calculated for $C_{16}H_{38}$.	Found.
266	267

The formula was further verified by its index of refraction.

It gave the index 1.4515, corresponding to the molecular refraction:—

Calculated for $C_{16}H_{38}$.	Found.
87.46	87.51

With the distillate 212° – 214° , 50 mm., the limit is reached of the solid hydrocarbons whose molecular weight can be determined by the freezing point method on account of the crystallization of the hydrocarbon before the benzol freezes. The molecular weights of solid higher members were determined by the boiling point method.

The results described in this paper defining the physical properties and formulae of the hydrocarbons separated from Pennsylvania petroleum differ in several essential particulars both from the hydrocarbons obtained by Krafft by decomposition of the monobasic acids with high molecular weights, and those formerly reported as among the constituents of Pennsylvania oil. It has been shown that the hydrocarbon at 196° is undecane, $C_{11}H_{24}$, and not dodecane as found by Pelouze and Cahours. Likewise the hydrocarbon at 216° proved to be dodecane and not tridecane. Since there was no method for ascertaining the molecular weights of these bodies at the time when they were separated by Pelouze and Cahours, and elementary analysis could only determine the series, it was only by analogy that the homologous members of the series could be guessed at. Since 182° was accepted at the boiling point of undecane, naturally dodecane and tridecane should fall into the heaps at 196° and 216° .

The boiling point of tridecane has been variously stated at 219° , 216° and 212° – 215° . But neither of these temperatures can be accepted as the boiling point of tridecane since its molecular weight is found to be that of the hydrocarbon boiling at 225° – 226° .

The hydrocarbon tetradecane boils at 236° – 238° , the same boiling point as was assigned to the tridecane separated by Pelouze and Cahours, but the specific gravity of tetradecane, 0.7812 at 20° is essentially lower than that found by Pelouze and Cahours, 0.809.

Pentadecane, boiling point 156° – 157° , is nearly the same in boiling point as the hydrocarbon separated by Pelouze and Cahours, boiling point 260° , although its specific gravity, 0.7896 at 20° , is much lower than they found, — 0.825 at 19° .

The boiling point of hexadecane is not very different from that given by Pelouze and Cahours, but its specific gravity is considerably lower. It does not differ in boiling point materially from hexadecane which Krafft obtained by heating palmitic acid, nor from that of hexadecane, boiling point 278° , obtained by Zincke from normal octyl iodide.* Since, however, the oils obtained by freezing out the solid hydrocarbons have specific gravities considerably higher than those of the original distillates, and apparently belong to another series, as shown by analysis and refraction indices, it is possible that the solid hydrocarbons held in solution in the oils have their boiling points depressed in the fractional distillation by which they were separated from the main body of the crude oil. Still, the molecular weights of the solid hydrocarbons correspond to definite formulas; for instance, from the distillate 300° – 301° , atmospheric pressure, octadecane was separated, in a practically pure form.

The less volatile portions of Pennsylvania petroleum consist of several series of hydrocarbons. The series C_nH_{2n} is liquid even at low temperatures, of higher specific gravity, and another is composed of solid hydrocarbons, of the series C_nH_{2n+2} .

In a former paper† it was shown that the high values assigned by Pelouze and Cahours as the specific gravity of the distillates separated by them from petroleum, indicated that their hydrocarbons were separated from Canadian petroleum. The same inference is supported by the high specific gravity of the hydrocarbons separated by Pelouze and Cahours boiling above 216° , as compared with the specific gravity of the hydrocarbons separated from Pennsylvania petroleum described in this paper.

* Ann. Chem. u. Pharm. 152, 15.

† These Proceedings, XXXII. 171.

After establishing a homologous series by analysis, evidently the only means available for Pelouze and Cahours to determine the molecular size of the hydrocarbons was to assume that a hydrocarbon constituted the chief portion of any distillates that collected in unusually large amounts, and to compute the series in unbroken order from the lower members.

Several attempts were made to ascertain the presence of the hydrocarbon $C_{20}H_{42}$; but the distillates between the limits 215° and 225° were small, and in none of them did the molecular weight obtained correspond to this formula.

HENEICOSANE, $C_{21}H_{44}$, AND LIQUID HYDROCARBON, $C_{21}H_{42}$.
FROM DISTILLATE 230° – 232° , 50 MM.

Larger quantities of distillates amounting to 200 grams collected at 230° – 232° , for the most part at 230° – 231° . The specific gravity of the unpurified distillate was 0.8321; after purification it gave 0.8230. A combustion of the purified oil gave the following percentages of carbon and hydrogen:—

0.1540 grm. of the oil gave 0.4813 grm. CO_2 and 0.1968 grm. H_2O .

	Calculated for		Found.
	$C_{21}H_{42}$	$C_{21}H_{44}$	
C	85.70	85.14	85.23
H	14.30	14.86	14.32

There was evidently some loss in this analysis, but the percentages are more satisfactory for the formula $C_{21}H_{42}$. It will be shown that this distillate was a mixture of a solid hydrocarbon with an oil of higher specific gravity. Its molecular weight was determined at the freezing point of benzol.

- I. 1.4807 grm. of the oil and 25.9125 grms. benzol gave a depression of $0^{\circ}.949$.
- II. 0.6845 grm. of the oil and 19.48 grms. benzol gave a depression of $0^{\circ}.579$.

Calculated for		Found.	
$C_{21}H_{42}$	$C_{21}H_{44}$	I.	II.
294	296	295	297.4

The index of refraction of this hydrocarbon was found to be 1.4608, corresponding to the molecular refraction:—

Calculated for $C_{21}H_{44}$	Found.
96.66	96.91

The molecular weight and molecular refraction show that this distillate is composed of a twenty-one carbon hydrocarbon, and the combustion and high specific gravity point to the series C_nH_{2n} .

A portion of the oil was cooled to -10° , filtered cold, the solid well pressed in filter paper, and crystallized from ether and alcohol. The ready solubility of these solid hydrocarbons in ether and insolubility in alcohol afford an easy means of purification. The melting point of the purified solid was 40° – 41° .

A combustion gave the following values for carbon and hydrogen:—

0.1353 grm. of the substance gave 0.4237 grm. CO_2 and 0.1778 grm. H_2O .

	Calculated for $C_{21}H_{44}$	Found.
C	85.13	85.39
H	14.87	14.72

The filtered oil gave as its specific gravity at 20° , 0.8424. The percentages of carbon and hydrogen were ascertained by a combustion:—

0.1498 grm. of the oil gave 0.4724 grm. CO_2 and 0.1898 grm. H_2O .

	Calculated for $C_{21}H_{44}$	Found.
C	85.70	85.98
H	14.30	14.08

Its molecular weight was determined at the freezing point of benzol.

0.9466 grm. of the oil and 21.01 grms. of benzol gave a depression of $0^\circ.737$.

Calculated for $C_{21}H_{44}$	Found.
294	299

DOCOSANE, $C_{22}H_{46}$, AND LIQUID HYDROCARBON, $C_{22}H_{44}$.
FROM DISTILLATE 240° – 242° , 50 MM.

After the thirtieth distillation, 150 grams collected at 240° – 242° , which gave as its specific gravity before purification 0.8341. After purification with fuming sulphuric acid its specific gravity was 0.8262. Combustions gave the following percentages of carbon and hydrogen:—

- I. 0.1538 grm. of the oil gave 0.4800 grm. CO_2 and 0.1992 grms. H_2O .
 II. 0.1560 grm. of the oil gave 0.4874 grm. CO_2 and 0.2024 grm. H_2O .
 III. 0.1362 grm. of the oil gave 0.4257 grm. CO_2 and 0.1788 grm. H_2O .

	Calculated for $\text{C}_{22}\text{H}_{44}$		I.	Found. II.	III.
C	85.70	85.16	85.09	85.21	85.25
H	14.30	14.84	14.40	14.42	14.59

The molecular weight was determined as follows: —

- I. 0.8367 grm. of the oil and 20.38 grms. benzol gave a depression of $0^\circ.642$.
 II. 2.5442 grms. of the oil and 21.91 grms. benzol gave a rise in boiling point of $0^\circ.9566$.

Calculated for $\text{C}_{22}\text{H}_{44}$	I.	Found. II.
308	313.4	311.3

The index of refraction was found to be 1.454 and the molecular refraction: —

Calculated for $\text{C}_{22}\text{H}_{44}$	Found.
101.27	100.7

The distillates in the vicinity of 240° , 50 mm., deposited no solid on standing at ordinary temperatures, but higher fractions all deposited solids. When cooled to 0° , the fraction 242° – 254° became nearly solid. After further cooling to -10° , the solid was filtered in a funnel surrounded with salt and ice, pressed in filter paper and crystallized from ether and alcohol. The solid melted at 43° , and further purified from gasoline, at 44° . Krafft gave $44^\circ.4$ as the melting point of the hydrocarbon $\text{C}_{22}\text{H}_{46}$. Its specific gravity at 60° was found to be 0.7796. A combustion gave proportions of carbon and hydrogen required for the series $\text{C}_n\text{H}_{2n+2}$.

0.1521 grm. of the solid gave 0.4721 grm. CO_2 and 0.2021 grm. H_2O .

	Calculated for $\text{C}_{22}\text{H}_{44}$		Found.
C	85.70	85.16	85.13
H	14.30	14.84	14.86

The quantity of the hydrocarbon was not sufficient for a determination of its molecular weight.

The filtered oil gave as its specific gravity at 20°, 0.8296, a value somewhat higher than that obtained before filtration. A combustion gave the following percentages of carbon and hydrogen: —

0.1505 grm. of the oil gave 0.4717 grm. CO₂ and 0.1937 grm. H₂O.

0.1411 grm. of the oil gave 0.4419 grm. CO₂ and 0.1819 grm. H₂O.

	Calculated for C ₂₃ H ₄₄ .	Found.	
C	85.70	85.49	85.41
H	14.30	14.31	14.32

These proportions correspond to the formula C₂₃H₄₄, which is supported by the high specific gravity.

The molecular weight of the filtered oil was also determined: —

1.0713 grm. of the oil and 19.60 grms. benzol gave a depression of 0°.858.

Calculated for C ₂₃ H ₄₄ .	Found.
308	312

The wide difference in specific gravity between the solid and liquid hydrocarbons at 240°–242°, 50 mm., point to different series. While the percentages of carbon and hydrogen given by analysis could not alone be depended on to prove the different series, the results of combustion with specific gravity are sufficient. The differences in theoretical composition of the two series are 0.5 of one per cent for carbon and for hydrogen. In combustions conducted under the most favorable conditions and with the greatest care, the different series may be shown in well purified materials. But with so many determinations, and the extreme care in details of the method, while the percentages obtained are sufficiently close to indicate the series, the results are not in all cases as close to the calculated percentages as should be reached in the greater precision of a few analyses.

TRICOSANE, C₂₃H₄₈, AND LIQUID HYDROCARBON, C₂₃H₄₆.
FROM DISTILLATE 258°–260°, 50 mm.

After the nineteenth distillation, 175 grams collected at 258°–260°, 50 mm., for the most part at 260°–261°, which deposited a considerable quantity of solid hydrocarbon on standing. The specific gravity of the unpurified distillate decanted from the solid was as follows: —

60°, 0.8341

70°, 0.8320

80°, 0.8310

The oil was agitated several times with concentrated sulphuric acid until the acid was not much colored, and washed with sodic hydrate and water, and finally with salt brine. On account of the high specific gravity of the oil some heavy solution such as brine or calcic chloride was necessary to separate the water and oil. The oil was dried for examination over calcic chloride and metallic sodium.

A combustion of the oil gave the following percentages of carbon and hydrogen :—

0.1508 grm. of the oil gave 0.4711 grms. CO_2 and 0.1945 grm. H_2O .

	Calculated for		Found.
	$\text{C}_{25}\text{H}_{40}$	$\text{C}_{25}\text{H}_{44}$	
C	85.70	85.18	85.21
H	14.30	14.82	14.33

A part of the carbonic dioxide was evidently lost, but the results point to the series C_nH_{2n} , which represents the composition of the oil, much the larger part of the distillate.

A portion of the distillate was cooled to -10° , and filtered cold to separate the crystalline solid. The solubility of the solid hydrocarbon seemed to diminish rapidly with lower temperatures, consequently a small proportion of the solid remains in the oil below -10° . After pressing and crystallizing from ether and alcohol, the solid melted at 45° . Krafft's hydrocarbon, $\text{C}_{28}\text{H}_{48}$, melted at $47^\circ.7$. Two determinations of its specific gravity at 60° gave (1) 0.7894, (2) 0.7900.

A combustion of the solid gave results for the series $\text{C}_n\text{H}_{2n+2}$:—

0.1515 grm. of the substance gave 0.4710 grm. CO_2 and 0.1989 grm. H_2O .

	Calculated for $\text{C}_{25}\text{H}_{48}$		Found.
C	85.20		85.06
H	14.80		14.64

A determination of its molecular weight at the boiling point of benzol was made :—

1.1208 grm. of the substance and 23.08 grms. benzol gave a rise of $0^\circ.412$.

Calculated for $\text{C}_{25}\text{H}_{48}$	Found.
324	327

The filtered oil gave as its specific gravity at 20°, 0.8569. It gave percentages of carbon and hydrogen required for the series C_nH_{2n} :—
0.1504 grm. of the oil gave 0.4711 grm. CO_2 and 0.1945 grm. H_2O .

	Calculated for		Found.
	$C_{25}H_{48}$	$C_{25}H_{48}$	
C	85.70	85.18	85.41
H	14.30	14.82	14.36

The molecular weight was determined at the freezing point of benzol:—
3.464 grms. of the oil and 26.06 grms. benzol gave a rise of 1°.0475.

Calculated for $C_{25}H_{48}$	Found.
322	325

The index of refraction was found to be 1.4714, from which was calculated the molecular refraction:—

Calculated for $C_{25}H_{48}$	Found.
105.87	105.31

**TETRACOSANE, $C_{24}H_{50}$, AND LIQUID HYDROCARBON, $C_{24}H_{48}$.
FROM DISTILLATE 272°-274°, 50 MM.**

After the nineteenth distillation, 150 grams collected at 272°-274°, 50 mm., that became partly solid on standing. The decanted oil gave as its specific gravity 0.8448 at 20°. A part of the distillate was then cooled to -10°, and the solid filtered cold under pressure.

The distillate was purified by treatment with successive portions of fuming sulphuric acid, until the acid was nearly colorless, then washed with sodic hydrate and a concentrated solution of calcic chloride, and dried over fused calcic chloride and sodium. Nearly one third of the volume was removed in purification. The purified oil then gave as its specific gravity at 20°, 0.8598, and at higher temperatures:—

60°, 0.8375	70°, 0.8366	80°, 0.8354
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A combustion of the purified oil gave percentages of carbon and hydrogen required for the series C_nH_{2n} .

0.1539 grm. of the oil gave 0.4769 grm. CO_2 and 0.2000 grm. H_2O .

	Calculated for		Found.
	$C_{24}H_{48}$	$C_{24}H_{50}$	
C	85.70	85.21	85.35
H	14.30	14.79	14.54

These percentages evidently support the formula $C_{24}H_{48}$.

A determination of the molecular weight of the liquid hydrocarbon gave at the boiling point of benzol a result required for $C_{24}H_{48}$.

2.0681 grms. of the oil and 25.78 grms. benzol gave a rise of $0^{\circ}.6096$.

Calculated for $C_{24}H_{48}$.	Found.
336	337.4

The index of refraction of the oil was found to be 1.4726, from which the following molecular refraction was calculated: —

Calculated for $C_{24}H_{48}$.	Found.
110.47	109.75

Specific gravity of the oil at 20° , 0.8582.

The solid separated by filtration melted at 48° . Krafft's hydrocarbon, $C_{24}H_{48}$, melted at 51° . It gave as its specific gravity the following values: —

60° , 0.7902	70° , 0.7893	80° , 0.7875
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With water at 4° these results reduce to 0.7742. The specific gravity given by Krafft to tetracosane at 4° was 0.7784, the same as that of the solid hydrocarbon which he separated from shale oil. The solid products from Pennsylvania oil show only slight variations in specific gravity. But the heavy oils show a decided increase in specific gravity with increase in molecular weight.

A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n+2} .

0.1433 grm. of the solid gave 0.4479 grm. CO_2 and 0.1895 grm. H_2O .

	Calculated for		Found.
	C_nH_{2n} .	$C_{24}H_{50}$.	
C	85.70	85.23	85.25
H	14.30	14.77	14.70

The molecular weight was determined at the boiling point of benzol.

Calculated for $C_{24}H_{50}$.	Found.
338	337

To ascertain whether the solid which separated at ordinary temperatures was identical with what remains in solution, a portion of the oil

was cooled to 0° , filtered at the same temperature, and the filtrate cooled to -10° and filtered under pressure at the same temperature. The three solids were carefully purified by crystallization from ether and alcohol and their melting points taken. The solid separated at ordinary temperatures melted at 48° , that separated at 6° melted at 51° - 52° , and that separated at -10° melted at 51° - 52° .

It is therefore evident that this distillate consists chiefly of one solid hydrocarbon, $C_{24}H_{50}$, and that the oil remaining liquid at -10° belongs to a different series.

PENTACOSANE, $C_{25}H_{52}$, AND LIQUID HYDROCARBON, $C_{26}H_{54}$.
FROM DISTILLATE 280° - 282° , 50 MM.

After the fifteenth distillation, 100 grams collected at 280° - 282° , 50 mm., which deposited a larger quantity of solid hydrocarbon than the lower distillates. This solid was separated from the oil and the latter was then cooled to 0° and filtered at the same temperature.

The specific gravity of the filtered oil at 20° was 0.8580.

A combustion gave the following values:—

0.1593 grm. of the oil gave 0.4997 grm. CO_2 and 0.2107 grm. H_2O .

	Calculated for $C_{26}H_{54}$.	Found.
C	85.70	85.55
H	14.30	14.67

The formula was established by its molecular weight, determined at the boiling point of benzol:—

3.9867 grms. of the oil and 30.19 grms. benzol gave a rise of $0^{\circ}.936$.

Calculated for $C_{26}H_{54}$.	Found.
364	362

A determination of the index of refraction gave 1.4725, which corresponded to the molecular refraction:—

Calculated for $C_{26}H_{54}$.	Found.
119.87	119.12

After crystallization from ether and alcohol, from which it separated in crystalline plates, the solid hydrocarbon gave percentages of carbon and hydrogen required for the series C_nH_{2n+2} .

0.1534 grm. of the substance gave 0.4787 grm. CO_2 and 0.2006 grm. H_2O .

	Calculated for $\text{C}_{27}\text{H}_{52}$.	Found.
C	85.25	85.09
H	14.75	14.53

A determination of its molecular weight verified the formula :—

1.7583 grm. of the substance, and 24.39 grms. benzol gave by the boiling point method a rise of $0^\circ.5231$.

Calculated for $\text{C}_{27}\text{H}_{52}$.	Found.
352	353.4

Melting point of the solid hydrocarbon, 53° – 54° .

HEXACOSANE, $\text{C}_{26}\text{H}_{54}$, AND LIQUID HYDROCARBON, $\text{C}_{27}\text{H}_{52}$.
FROM DISTILLATE 292° – 294° , 50 mm.

After the fifteenth distillation, 100 grams collected at 292° – 294° , 50 mm., which deposited a considerable quantity of solid crystalline hydrocarbon. These crystals were filtered, pressed, and purified by crystallization from ether and alcohol. Melting point, 58° . The specific gravity of this hydrocarbon was determined as follows:—

60° , 0.7977 70° , 0.7956 80° , 0.7943

A combustion of the solid gave the following percentages of carbon and hydrogen :—

0.1508 grm. of the substance gave 0.4709 grm. CO_2 and 0.2033 grm. H_2O .

	Calculated for $\text{C}_{26}\text{H}_{54}$.	Found.
C	85.24	85.17
H	14.76	14.98

The molecular weight was ascertained at the boiling point of benzol.

1.2754 grm. of the substance and 24.2827 grms. benzol gave a rise of $0^\circ.416$.

Calculated for $\text{C}_{27}\text{H}_{54}$.	Found.
366	364

On cooling the original distillate to -10° , it formed a thick pasty mass. It was filtered under pressure, keeping cold. The filtered crystals were pressed, and crystallized from ether and alcohol. Melting point, 58° . The solids pressed out from the fractions from 288° to 302° , 50 mm., showed very slight variations in melting points.

288°-290°,	56°.	300°-304°,	59°-60°.
294°-296°,	58°.	302°-304°,	59°-60°.

The oil filtered under pressure was very thick and viscous. Its specific gravity at 20° was 0.8688. A combustion gave the following percentages of carbon and hydrogen:—

0.1500 grm. of the oil gave 0.4750 grm. CO_2 and 0.1812 grm. H_2O .

	Calculated for $\text{C}_{27}\text{H}_{52}$.	Found.
C	86.17	86.36
H	13.83	13.43

Its molecular weight at the boiling point of benzol corresponded to the formula $\text{C}_{27}\text{H}_{52}$.

3.6506 grms. of the oil and 25.80 grms. benzol gave a rise of $0^{\circ}.964$.

Calculated for $\text{C}_{27}\text{H}_{52}$.	Found.
376	376.2

The index of refraction corresponded to the same formula.

The index was found to be 1.4722, and the molecular refraction:—

Calculated for $\text{C}_{27}\text{H}_{52}$.	Found.
122	121.4

OCTOCOSANE, $\text{C}_{28}\text{H}_{58}$, AND LIQUID HYDROCARBON, $\text{C}_{28}\text{H}_{54}$.
FROM DISTILLATE 310° - 312° , 50 MM.

After the tenth distillation 75 grams collected at 310° - 312° , from which a considerable quantity of crystals collected above the oil on standing. The oil separated from the crystals was then cooled to -10° and filtered cold under pressure. The solid was pressed and purified by crystallization from ether and alcohol. Melting point 60° . Its specific gravity was determined as follows:—

70°, 0.7945	80°, 0.7927	90°, 0.7911
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A combustion gave the following percentages of carbon and hydrogen:—

0.1508 grm. of the substance gave 0.4703 grm. CO_2 and 0.2032 grm. H_2O .

	Calculated for $\text{C}_{28}\text{H}_{58}$.	Found.
C	85.28	85.07
H	14.72	14.97

The molecular weight at the boiling point of benzol corresponded to the formula $\text{C}_{28}\text{H}_{58}$.

3.070 grms. of the solid hydrocarbon and 26.21 grms. benzol gave a depression of $0^\circ.7538$.

	Calculated for $\text{C}_{28}\text{H}_{58}$.	Found.
	394	399

The very thick oil separated by filtration gave as its specific gravity at 20° , 0.8694. A combustion gave percentages of carbon and hydrogen required for the series, $\text{C}_n\text{H}_{2n-2}$.

0.1500 grm. of the oil gave 0.4729 grm. CO_2 and 0.1836 grm. H_2O .

	$\text{C}_{28}\text{H}_{58}$	Calculated for $\text{C}_{28}\text{H}_{58}$	$\text{C}_{28}\text{H}_{54}$	Found.
C	85.28	85.70	86.02	85.96
H	14.72	14.30	13.98	13.60

The molecular weight was found at the boiling point of benzol.

- I. 2.6792 grms. of the oil and 29.85 grm. benzol gave a rise of $0^\circ.5826$.
 II. 1.9196 grms. of the oil and 27.98 grm. benzol gave a rise of $0^\circ.4459$.

Calculated for $\text{C}_{28}\text{H}_{54}$.	I.	Found.	II.
392	396		394.4

The index of refraction was found to be 1.480, which corresponds to the molecular refractions:—

Calculated for $\text{C}_{28}\text{H}_{58}$.	Found.
127	126.78

It will be observed that the two liquid hydrocarbons last described have been shown to belong to a series $\text{C}_n\text{H}_{2n-2}$. Results already ob-

tained but not yet published indicate that the same series of hydrocarbons constitute the less volatile portions of Canadian petroleum, and probably also of Ohio petroleum. Results already published show that the less volatile distillates from California and Texas petroleum are composed of the same series and other series still poorer in hydrogen.

The unexpected appearance of the series C_nH_{2n-2} in Pennsylvania petroleum suggests a closer relationship between this petroleum and the heavier oils from other fields, such as those in Texas and California, than was suspected. To gain further information concerning the heavier portions of Pennsylvania oil, we allowed three kilos of the sample from which the hydrocarbons described in this paper were prepared, to evaporate spontaneously in the air in a strong draught, but with no application of heat. At the end of thirty days there remained one kilo that gave as its specific gravity 0.8620, practically the same as that of $C_{28}H_{54}$, 0.8694. A combustion gave percentages of carbon and hydrogen required for the series C_nH_{2n-2} . A distillation showed that 65 per cent of the residual oil was composed of hydrocarbons above $C_{16}H_{30}$. The composition of these hydrocarbons will be ascertained in connection with the study of natural and commercial paraffine, which is now in progress.

This interesting relation, and others between the numerous petroleum from different oil fields that have been examined in this laboratory will be presented more at length in a later paper.

As a general summary of the results described in this paper, hydrocarbons have been identified as shown in table on opposite page.

It appears that the liquid hydrocarbon $C_{28}H_{54}$ in fraction 310° – 312° has the same number of carbon atoms as the solid hydrocarbon octocosane in the same fraction. In this respect the hydrocarbons in this fraction differ from those in the two preceding fractions, in each of which the liquid hydrocarbon is one carbon higher than the solid constituent. Determinations of the molecular weights of hydrocarbons with high carbon content can only be made by the boiling-point method; and even with the greatest care in manipulation, this method is somewhat uncertain for high molecular weights of solid hydrocarbons, for the reason that the rise in boiling points diminishes with the increase in molecular weight. With oils there is less difficulty. For instance, the molecular weight, 376.2, of the liquid hydrocarbon $C_{27}H_{52}$, given on page 592, is one of five closely concordant determinations by different persons. As an illustration of the care necessary in details, heating with a lamp supplied with gas from the laboratory mains is so irregular on account of variation in gas pressure that the gas must be supplied from a tank under water

Name.	Symbol.	Boiling Point.	Melting Point.
Tridecane	$C_{13}H_{28}$	226°	
Tetradecane	$C_{14}H_{30}$	236°-238°	
Pentadecane	$C_{15}H_{32}$	256°-257°	
Hexadecane	$C_{16}H_{34}$	274°-275°	
Heptadecane	$C_{17}H_{36}$	288°-289°	10°
Octadecane	$C_{18}H_{38}$	300°-301°	20°
Nonadecane	$C_{19}H_{40}$	210°-212°, 50 mm.	33°-34°
Heneicosane	$C_{21}H_{44}$	230°-231°, "	40°-41°
Hydrocarbon, liquid at -10°	$C_{22}H_{44}$	240°-242°, "	
Docosane	$C_{22}H_{46}$		44°
Hydrocarbon, liquid at -10°	$C_{23}H_{46}$	258°-260°, "	
Tricosane	$C_{23}H_{48}$		45°
Hydrocarbon, liquid at -10°	$C_{24}H_{48}$	272°-274°, "	
Tetracosane	$C_{24}H_{50}$		48°
Hydrocarbon, liquid at -10°	$C_{26}H_{52}$	280°-282°, "	
Pentacosane	$C_{25}H_{52}$		53°-54°
Hydrocarbon, liquid at -10°	$C_{27}H_{52}$	292°-294°, "	
Hexacosane	$C_{26}H_{54}$		58°
Hydrocarbon, liquid at -10°	$C_{28}H_{54}$	310°-312°, "	
Octocosane	$C_{28}H_{58}$		60°

pressure. Much attention has been given to these determinations, especially by Messrs. O. J. Sieplein and R. P. Cushing.

The preparation of the distillates described in this paper was begun December 1, 1896, by Mr. A. S. Kittelberger, who distilled 56 kilos of Pennsylvania crude oil. The distillations were later continued by different assistants. The following gentlemen have also aided in the purification, examination, and analysis of these hydrocarbons: Messrs. Shaw, Latimer, R. P. Cushing, Dr. E. J. Hudson, and O. J. Sieplein. To the latter especially is due the analysis and identification of the chlorine derivatives of the hydrocarbons.